D4

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-106333
(43)Date of publication of application : 20.04.1999

(51)Int.Cl. A61K 31/015
A61K 9/19
A61K 31/07
A61K 31/355
A61K 31/59
A61K 31/595

(21)Application number : 09-282739
(22)Date of filing : 30.09.1997

(71)Applicant : KURARAY CO LTD
(72)Inventor : MORI TOSHIKI
MIMURA HITOSHI

(54) PRODUCTION OF POWDER CONTAINING FAT-SOLUBLE VITAMIN AND/ OR CAROTENOID

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method capable of reducing an amount of gelatin used and lowering the temperature of heating treatment in a method for producing powder which contains a fat-soluble vitamin and/or carotenoid and does not collapse even in hot water.
SOLUTION: This method for producing power comprises changing an emulsion comprising (a) a fat-soluble vitamin and/or carotenoid, (b) gelatin in which pH measured by a method specified in JIS K6503 is 2-5, (c) reducing saccharide, (d) starch and (e) water to droplet, catching the droplet in starch powder to form fine particles and subjecting the resultant fine particles to heat treatment at 45-85° C.

(SCOPE OF PATENT CLAIMS)

(CLAIM 1) Method of manufacturing a powder containing fat-soluble vitamin and/or carotenoid, whereby an emulsion consisting of

a) fat-soluble vitamin and/or carotenoid,

b) gelatin with a pH of 2–5 as measured by the method prescribed in JIS K6503,

c) reducing sugar,

d) starch, and

e) water

is changed to droplets, said droplets are trapped in starch powder to form particulates, and the resultant particulates are heat-treated at 45°C–85°C.

(DETAILED DESCRIPTION OF THE INVENTION)

(0001)

(TECHNICAL FIELD OF THE INVENTION) The present invention relates to a method of manufacturing a powder containing fat-soluble vitamin and/or carotenoid (these are hereinafter sometimes referred to as the active ingredients).

(0002)

(PRIOR ART) Fat-soluble vitamins such as vitamin A acetate or carotenoids such as β-carotene have prior to now been widely used as additives in animal feed or food products. Fat-soluble vitamins or carotenoids are compounds whose activity is prone to degrading due to the effect of heat or oxygen, so they are generally prepared in the form of powders embedded in a matrix such as gelatin or the like in order to sustain their activity under the conditions by which the animal feed or food product is to be processed. In recent years, a need has emerged for these powders to have the property of not disintegrating in hot water.

(0003) Examples of known methods of manufacturing a powder containing fat-soluble vitamin or carotenoid that does not disintegrate in hot water include:

① A method whereby an emulsion consisting of fat-soluble vitamin and/or carotenoid, water, gelatin and a reducing sugar such as dextrose or fructose is changed to droplets, the resultant droplets are trapped in starch powder to form particulates, and the resultant particulates are heat treated at roughly 90–180°C, preferably 105–150°C (see the specification of U.S. Patent No. 4,670,247).

② A method whereby a basic emulsion consisting of amino compound in addition to fat-soluble vitamin and/or carotenoid, water, gelatin, starch and a reducing sugar is changed to droplets, the resultant droplets are trapped in starch powder to form particulates, and the resultant particulates are heat treated at roughly 60–180°C, preferably 70–130°C (see Japanese Unexamined Patent Application Publication H6-65062).

(0004)

(PROBLEM TO BE SOLVED BY THE INVENTION) In the aforesaid method ①, heat treatment forms a cross-link between the carbonyl group in the sugar and the free amino group in the gelatin molecule, thus causing the property of not disintegrating in hot water to be expressed in the resultant powder. With this method, to intentionally cause the formation of a cross-link between the carbonyl group in the sugar and the free amino group in the gelatin molecule, a relatively large quantity of costly gelatin must be used (35–45% by weight relative to the dry weight of the powder). Furthermore, because the active ingredients of fat-soluble vitamin and/or carotenoid are, as stated previously, compounds that degrade easily due to the effect of heat, it would be desirable to avoid as much thermal stress as possible during heat treatment. Because the temperature of the heat treatment used in the aforesaid method ① is 90°C or greater, it would be desirable that the aforesaid cross-link be formed at a lower temperature. With the aforesaid method ②, on the other hand, a smaller amount of gelatin is used than the aforesaid method ①, but a relatively large amount of amino compound must be added when preparing the emulsion (10–35% by weight relative to gelatin). Furthermore, the aforesaid method ② states that a temperature of 60°C or greater can be used for heat treatment, but in the embodiments the specific temperature used is 100°C or greater, so it would be desirable to be able to form the aforesaid cross-link by heat-treatment at a lower temperature.

(0005) The objective of the present invention is to provide a method of manufacturing a powder containing fat-soluble vitamin and/or carotenoid that does not disintegrate in hot water, that is able to reduce the amount of gelatin used without adding a component such as amino compound or the like, and that reduces the thermal stress during heat treatment.

(0006)

(MEANS FOR SOLVING THE PROBLEM) The inventors completed the present invention after conducting a research following the discovery that using a designated gelatin solves the aforesaid problems with the prior-art methods of manufacturing a powder containing fat-soluble vitamin and/or carotenoid. In short, the present invention is a method of manufacturing a powder containing fat-soluble vitamin and/or carotenoid, whereby an emulsion consisting of

a) fat-soluble vitamin and/or carotenoid,

b) gelatin with a pH of 2–5 as measured by the method prescribed in JIS K6503,

c) reducing sugar,

d) starch, and

e) water

is changed to droplets, said droplets are trapped in starch powder to form particulates, and the resultant particulates are heat-treated at 45°C–85°C.

(0007)

(EMBODIMENTS OF THE INVENTION) First, in the present invention, emulsions composed of the aforesaid components a)–c) are prepared. Examples of fat-soluble vitamin (aforesaid

component a)) used in the present invention include A vitamins such as vitamin A acetate, vitamin A palmitate, vitamin A (retinol), vitamin A aldehyde (retinol) and vitamin A acid; D vitamins such as cholecalciferol (vitamin D_3), ergocalciferol (vitamin D_2), 1α,25-dihydroxycholecalciferol (active vitamin D_3) or derivatives thereof; E vitamins such as α-tocopherol, 5,7,8-trimethyl tocotrienol; and K vitamins such as 2-farnesyl-3-methyl-1,4-naphthoquinone (vitamin K_2) and 2-methyl-1,4-naphthoquinone (vitamin K_3). Furthermore, examples of carotenoid (aforesaid component a)) used in the present invention include β-carotene, cantaxanthin, astaxanthin and lutein.

(0008) Furthermore, the gelatin (aforesaid component b)) used in the present invention must have a pH of 2–5 as measured by the method prescribed in JIS K6503. In the present invention, using a gelatin wherein the aforesaid pH is 2 or less will reduce the stability of the fat-soluble vitamin and carotenoid, causing the activity of the powder to decline during manufacture. On the other hand, using a gelatin wherein the aforesaid pH is greater than 5 in the present invention will require that the thermal stress be increased during heat treatment in order to obtain a powder that will not disintegrate even in hot water, which is not preferable. It is preferable that the pH of the gelatin be 4–5. Moreover, the phrase "will not disintegrate even in hot water" used in the present invention means that the active ingredients in the resultant powder do not elute into boiling water even after being in this water for 3 minutes.

(0009) In the present invention, it is believed that the use of a gelatin with the appropriate acidity value activates the carbonyl group in the reducing sugar, and the interaction with the free amino group in the gelatin renders possible the expression of the property of "not disintegrating even in hot water" even when heat-treatment is performed at a low temperature.

(0010) Gelatin known as type A or type B is generally easy to obtain, and either of these types may be used. If using a gelatin whose pH is outside of the aforesaid range, simply adjust the pH to within the aforesaid range using mineral acid such as hydrochloric acid, sulfuric acid, sodium bisulfate, potassium bisulfate, phosphoric acid, disodium phosphate, dipotassium phosphate or salt thereof; or an organic acid such as acetic acid or propionic acid. Adjustment of the pH of the gelatin is ordinarily performed by adding the desired quantity of mineral acid or salt thereof or organic acid to the gelatin in the presence of water.

(0011) Moreover, when preparing the emulsion, the desired quantity of this mineral acid or organic acid can be added separately from the gelatin. The present invention also subsumes such an embodiment. In addition, in the present invention, there is no particular limit on the bloom value of the gelatin that is used, the bloom value being a value that expresses the hardness of the said.

(0012) The quantity of gelatin used is normally within the range of 0.5–1.5-fold by weight relative to the active ingredients, and preferably within the range of 0.7–1.3-fold by weight relative to the active ingredients.

(0013) Examples of the reducing sugar (aforesaid component c)) used in the present invention include glucose, fructose, arabinose, xylose, ribose, lactose, maltose and cellobiose. A single type of reducing sugar may be used, or a mixture of two or more such as invert sugar (a mixture of glucose and fructose) or a mixture of glucose and xylose can be used. The quantity of reducing sugar used is normally 0.7–2-fold by weight relative to the active ingredients.

(0014) Examples of starch (aforesaid component d)) that can be used in the present invention include raw starch collected from potato or corn; or modified starch such as oxidized starch, acetylated starch, methylated starch and carboxymethylated starch. Starch in the present invention is surmised to serve the purpose of reducing the quantity of gelatin used. The quantity of starch used is normally within the range of 0.1–1-fold by weight relative to the active ingredients.

(0015) There is no particular limit on the quantity of water (aforesaid component e)) used in the present invention, but the quantity is normally within the range 1–10-fold by weight relative to the active ingredients.

(0016) In the present invention, antioxidant such as 2,6-di-t-butyl hydroxytoluene (BHT), 2-t-butyl-4-hydroxyanisole (BHA) or 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline (ethoxyquin) may be used together with the aforesaid components a)–e) as necessary for the purpose of sustaining the activity of the active ingredients.

(0017) In the present invention, any known method may be used as the method of preparing the emulsion consisting of the aforesaid components a)–e), one example method being to add fat-soluble vitamin and/or carotenoid, reducing sugar, starch and other components used as needed such as antioxidants to an aqueous solution of gelatin with a pH of 2–5 and then emulsifying using a known means such as a homogenizer. Preparation of the emulsion is normally conducted at room temperature to 80°C, but preferably is conducted at 50°C–60°C.

(0018) Next, in the present invention, the emulsion obtained by the aforesaid method is changed to droplets, and particulates are formed by trapping said droplets in starch powder. Any known method can be used as the method of changing the emulsion obtained by the aforesaid to droplets, for example spraying the aforesaid emulsion at a pressure of 15–30 kg/cm^2 from a spray nozzle with an aperture of 1.0–2.0 mm. There are no particular restrictions on the method of trapping the droplets generated by the aforesaid method in the starch powder; any known method can be used. To cite

specific examples, the aforesaid droplets can be dropped onto a fixed bed of starch powder, or the aforesaid emulsion can be sprayed onto a stream of air in which the starch powder has been dispersed, etc.

(0019) The same examples cited in the description of emulsion component d) can be cited as specific examples of the starch used here, and within the cited range, any starch different from that used as component d) of the emulsion can be used. It is preferable that the size of the starch powder be within a range that will actually fully pass through a 200 mesh (aperture: 74 μ) sieve.

(0020) Particulates obtained by the aforesaid method normally have a size within a range that will actually fully pass through a 10 mesh sieve but be supported on a 200 mesh sieve, but it is preferable that these have a size within a range that will actually fully pass through a 20 mesh sieve but be supported on a 170 mesh sieve.

(0021) In the present invention, the particulates obtained by the aforesaid method are heat-treated at 45°C–85°C. If the temperature at which heat-treatment is performed here is less than 45°C, it will not be possible to obtain a powder that does not disintegrate in hot water. If the temperature at which heat-treatment is performed is higher than 85°C, the increased thermal strain will make the active ingredients prone to degrading. It is preferable that the temperature at which heat-treatment is performed is within the range of 60–85°C.

(0022) Said heat-treatment removes the moisture from the particulates, causing these to become dry as well as expressing the property of not disintegrating even in hot water due to the interaction between the carbonyl group in the reducing sugar and the free amino group in the gelatin.

(0023) Here, heat-treatment of the particulates can be performed using a well-known method, but it is easier to do so using an ordinary drying device. Normally, on the order of 10 minutes to 30 hours is required for heat-treatment, although this time will differ depending on the temperature at which heat-treatment is performed as well as the type of reducing sugar used. Moreover, using as the reducing sugar a sugar such as xylose or ribose that can easily possess a free aldehyde group makes it possible to express the property of not disintegrating even in hot water by means of relatively low-temperature and short-duration heat-treatment.

(0024) In prior-art methods, drying was considered a separate process from heat treatment, but in the present invention, heat-treatment is performed in the same process as drying, and within about the same temperature range as the temperature used for drying, simplifying the process of manufacturing a powder containing fat-soluble vitamin and/or carotenoid.

(0025) In the present invention, heat-treatment can be performed at normal temperature or decompressed or pressurized. Furthermore, in the present invention, to prevent the resultant powders from sticking to one another, it is preferable that the heat-treatment be performed such that the particulates are streamed by a method such as rotation, vibration or stirring.

(0026) It is preferable that the powder containing fat-soluble vitamin and/or carotenoid obtained by the aforesaid method be separated from the surplus starch powder. This separation operation can be performed by a well-known method such as using an appropriately-sized sieve or dispersing the starch powder with a stream of air or the like, but in the present invention, by performing the aforesaid heat-treatment using a drying device consisting of a fluid bed and a stream of temperature-adjusted dry air or nitrogen, the surplus starch can be isolated at the same time as heat-treatment, making it possible to simplify the operations when manufacturing a powder containing fat-soluble vitamin and/or carotenoid.

(0027) The powder obtained by the method in the present invention normally has a size in the range of 50–800 μm, does not disintegrate even in hot water, and sustains the activity of the active ingredients, so it can be used effectively as an additive in animal feed or food products.

(0028)

(EMBODIMENTS) The present invention will be described in specific detail below by way of embodiments, but the present invention is not limited to the following embodiments.

(0029) Embodiment 1

4.3 kg oxidized starch and 12 kg glucose were added to a mixture of 10 kg gelatin (type A, 119 bloom, moisture content 11.9%) with a pH of 4.4 as measured by the method prescribed in JIS K6503 and 41 kg water and stirred at 60°C. 8 kg vitamin A acetate dissolved by heating (2.9 million IU/g) and 2.4 kg ethoxyquin were added to the resultant mixture, which was then emulsified for 2 minutes at 60°C using a homogenizer, producing an emulsion containing vitamin A acetate. The resultant emulsion was sprayed from a spray nozzle (aperture: 1.5 mm) at a pressure of 22 kg/cm^2 into a 30°C stream of dried air made by dispersing acetylated starch powder in a proportion of 200 g /m^3, producing particulates consisting of emulsion droplets whose surfaces are coated in acetylated starch. The particulates that fell down were introduced into a fluidized bed desiccator, where they were heat-treated for 10 hours using 80°C dry air, producing 29.8 kg of powder containing vitamin A acetate (vitamin A acetate content: 480,000 IU/g). Moreover, during this heat-treatment, surplus acetylated starch powder was removed by a stream of dry air. Furthermore, when the resultant powder was placed in water and boiled for 3 minutes, aside from swelling slightly, it retained its shape and there was no sign of elution of vitamin A acetate into the boiling water.

(0030) Embodiment 2

The same operations as Embodiment 1 were performed, except that instead of using 12 kg glucose as in Embodiment 1, 12 kg fructose was used, producing 28 kg of powder containing vitamin A acetate (vitamin A acetate content: 480,000 IU/g). When the resultant powder was placed in water and boiled for 3 minutes, aside from swelling slightly, it retained its shape and there was no sign of elution of vitamin A acetate into the boiling water.

(0031) Embodiment 3
The same operations as Embodiment 2 were performed, except that instead of using 12 kg fructose as in Embodiment 2, 12 kg xylose was used, producing 28.5 kg of powder containing vitamin A acetate (vitamin A acetate content: 490,000 IU/g). When the resultant powder was placed in water and boiled for 3 minutes, aside from swelling slightly, it retained its shape and there was no sign of elution of vitamin A acetate into the boiling water.
(0032) Embodiment 4
The same operations as Embodiment 2 were performed, except that instead of using 12 kg fructose as in Embodiment 2, 10 kg glucose and 2 kg xylose were used, producing 30.2 kg of powder containing vitamin A acetate (vitamin A acetate content: 480,000 IU/g). When the resultant powder was placed in water and boiled for 3 minutes, aside from swelling slightly, it retained its shape and there was no sign of elution of vitamin A acetate into the boiling water.
(0033) Comparative Example 1
The same operations as Embodiment 1 were performed, except that instead of using 12 kg glucose as in Embodiment 1, 12 kg saccharose (sucrose, non-reducing sugar) was used, producing 29 kg of powder containing vitamin A acetate (vitamin A acetate content: 480,000 IU/g). When the resultant powder was placed in boiling water, it immediately disintegrated, producing a turbid liquid.
(0034) Embodiment 5
0.46 kg acetic acid was added to a mixture of 10 kg gelatin with a pH of 5.6 as measured by the method prescribed in JIS K6503 (type B, 121 bloom, moisture content 11.7%) and 44 kg water and heated at 60°C, producing a 54.4 kg aqueous solution of gelatin with a pH of 4.3 as measured by the method prescribed in JIS K6503. 4 kg oxidized starch, 12 kg glucose, 15 kg vitamin A acetate (2.9 million IU/g) and 4.5 kg ethoxyquin were added to the resultant aqueous solution, after which, by the same operations as Embodiment 1, an emulsion was prepared and sprayed into a stream of dry air in which was dispersed acetylated starch powder, and the resultant particulates were heat-treated, producing 35.5 kg of powder containing vitamin A acetate (vitamin A acetate content: 680,000 IU/g). When the resultant powder was placed in water and boiled for 3 minutes, aside from swelling slightly, the powder retained its shape and there was no sign of elution of vitamin A acetate into the boiling water.
(0035) Comparative Example 2
The same operations as Embodiment 2 were performed, except that no acetic acid was added as in Embodiment 5, producing 30.5 kg of powder containing vitamin A acetate (vitamin A acetate content: 670,000 IU/g). When the resultant powder was placed in boiling water, it immediately disintegrated, producing a turbid liquid.
(0036) Embodiment 6
The same operations as Embodiment 1 were performed, except that instead of using 8 kg vitamin A acetate as in Embodiment 1, 8 kg β-carotene was used, producing 33 kg of powder containing β-carotene.
(0037) When the resultant powder was placed in water and boiled for 3 minutes, aside from swelling slightly, the powder retained its shape and there was no sign of elution of β-carotene into the boiling water.
(0038)
(EFFECT OF THE INVENTION) According to the present invention, powder that contains fat-soluble vitamin and/or carotenoid and does not disintegrate in hot water can be manufactured without impairing the activity of the active ingredients. Additionally, according to the present invention, when manufacturing said powder, the amount of gelatin used can be reduced and the temperature of heat-treatment can be reduced without needing to add components such as amino compounds.

Continued from front page

(51)Int.Cl.[6] Identification Codes FI
A 61 K 31/595 A 61 K 9/14 E